Final Report On "Electronic Structure of Lithium Battery Materials"
DEFG0203ER15425, P.I. Prof. Peter Rez, ASU.

We have continued our work on$Li_x(NiMn)_{0.5}O_2$ cathode materials and extended the techniques to the more complex $Li_x(NiMnCo)_{0.333}O_2$ system. An important development was the application of the charge partitioning scheme due to Bader[1] to uniquely attribute charge to a particular atom. This confirmed that as lithium is removed most of the charge compensation takes place on the oxygen atoms. Since the top of the valence band is mainly oxygen 2p states, the Fermi level then moves to lower energies. Transitions into the empty oxygen p states at the top of the valence band give rise to the Oxygen K edge pre peak that we have observed in both Li_xCoO_2 and $Li_x(NiMn)_{0.5}O_2$.

Our calculations show the similar behaviour for $Li_x(NiMnCo)_{0.333}O_2$. There are no changes in the charge associated with Ni, Mn or Co on delithiation which is consistent with the EELS measurements of the L_{23} "white lines". A manuscript on the theoretical aspects of charge transfers and band structure changes in a range of transition metal oxides will be submitted in the near future.

For most of the final period of this grant we have been working on Li_xFePO_4 , a new cathode material which is environmentally more friendly and less costly than Li_xCoO_2 The intermediate compositions arise from a mixture of $LiFePO_4$ (mineral name triphylite) and $FePO_4$ (mineral name heterosite). The charge compensation mechanism is also of interest in these materials. The presence of a pre peak on the oxygen K edge for triphylite indicates that there are some similarities to Li_xCoO_2 with an emptying of electrons from the oxygen p states at the top of the valence band. However the changes observed in the Fe L_{23} white lines show that Fe changes from Fe^{2+} to Fe^{3+} as Li is removed. Our Caltech collaborators provided spectra at about 1.5 eV resolution showing a change in the L_3/L_2 ratio and a peak shift which were able to match with atomic multiplet calculations with a crystal field splitting, 10Dq, of 3.0eV. Ceder's group[2,3] have used the LSDA (+U) theory to calculate the open circuit voltages as a function of Li concentration. No rigorous criteria were put forward for selecting a given value of U and furthermore U should strictly depend on the charge state of the Fe ion. We performed detailed calculations of both the Fe d and O p densities of states for both $FePO_4$ and $LiFePO_4$ while varying U and considering the possibility of both ferromagnetic and antiferromagnetic ordering. At the resolution of the Caltech experiments no differences could be observed. However if higher resolution energy loss spectra could be recorded it seemed that it would be possible to determine if the values of U suggested by Zhou et al[2,3] were consistent with EELS measurements (see Fig 1). We recorded spectra using the monochromated TEM with EELS at the NCEM Berkeley. The effects are most noticeable on the Fe L edge and although we were able to record spectra with 0.2 eV resolution, they were still dominated by atomic multiplet effects (see Fig 2). The agreement with our atomic multiplet calculations was much improved using a more realistic value for 10Dq of about 1.5eV. From measurements of the oxygen pre peak and the ratio of white line to continuum used in conjunction with our VASP GGA calculations we concluded that both the oxygen and the iron atoms contribute equally to charge compensation as lithium is removed.

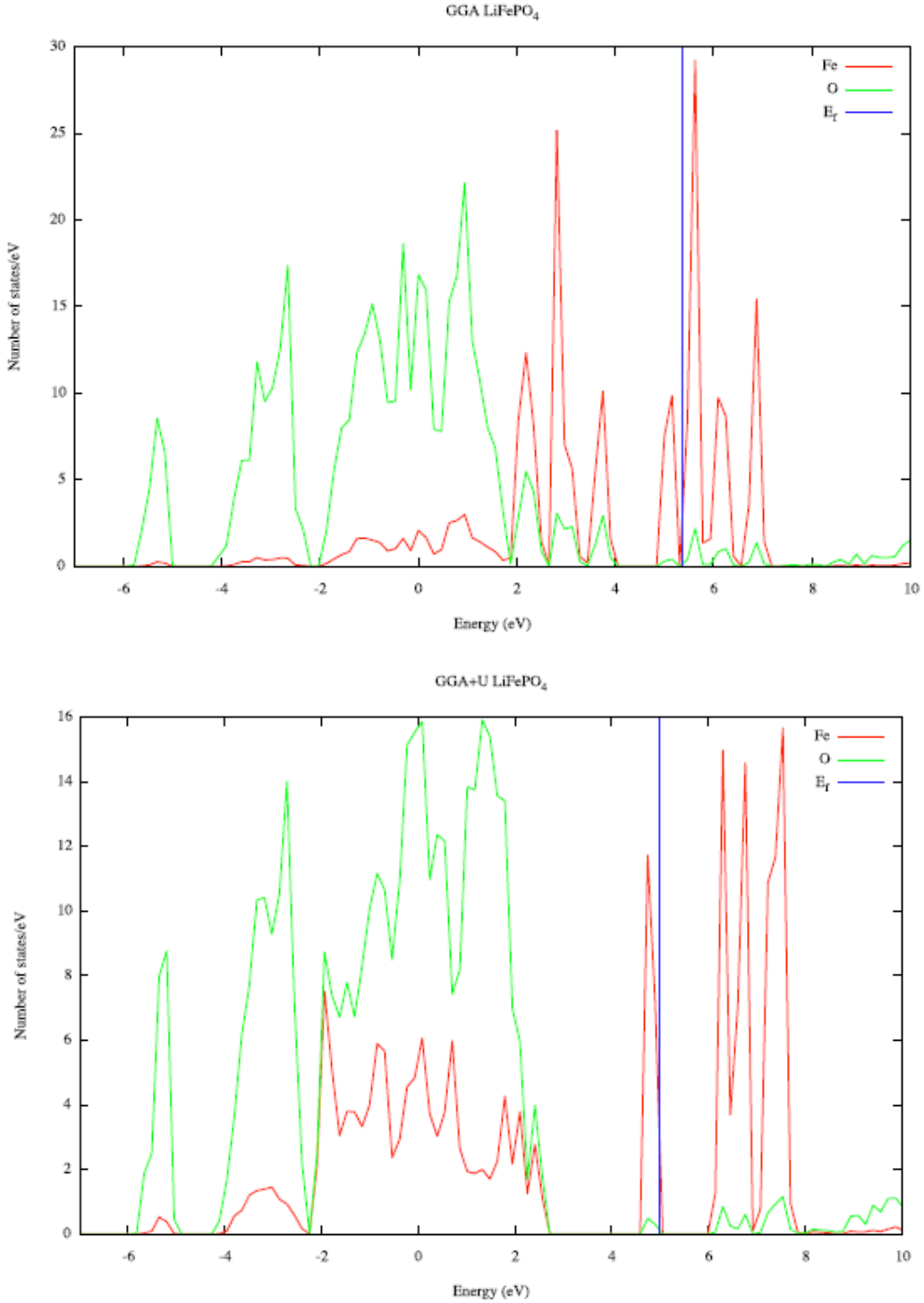
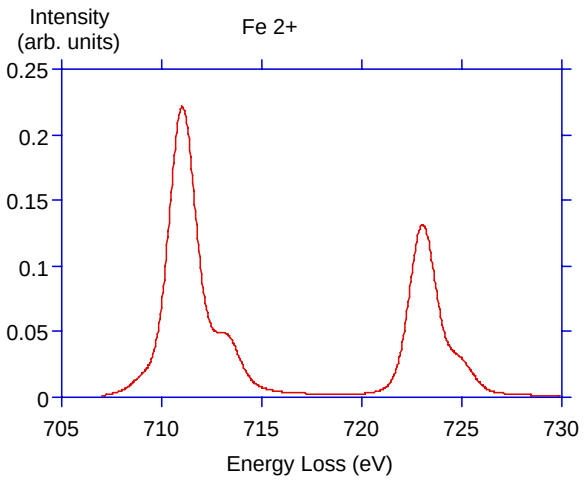
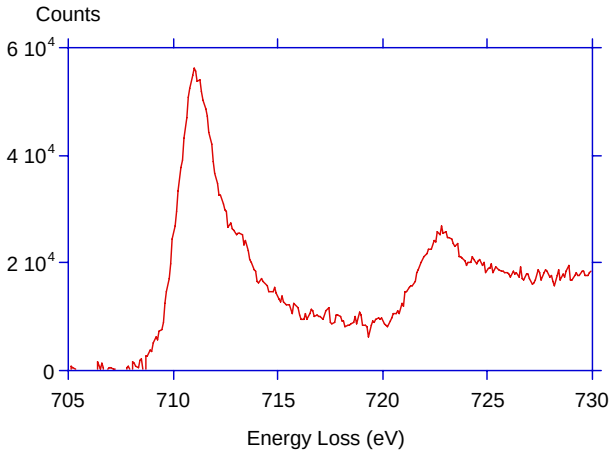


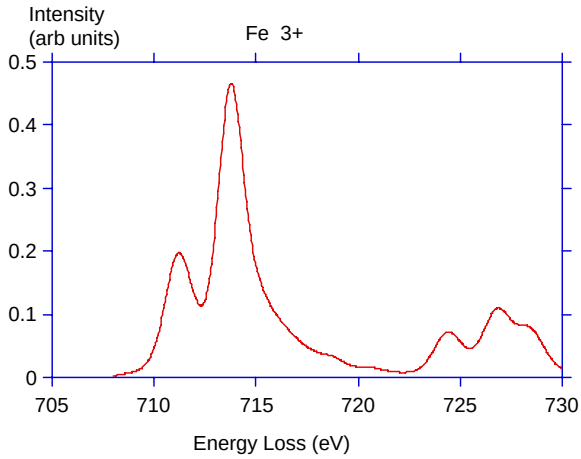
Fig 1. VASP GGA (Generalized Gradient Approximation) Calculations showing the Effect of the On Site energy U on Densities of States (O p, Fe d) for $LiFePO_4$



Multiplet Calculation showing Fe L edge for Fe^{2+}



High Resolution (nominally 0.2 eV) EELS measurement of Fe L from $LiFePO_4$



Multiplet Calculation showing Fe L edge for Fe^{3+}
Figure 2

Publications From This Grant (Not Previously Reported)

"Local Electronic Structure of Layered $Li_xNi_{0.333}M_{0.33}Co_{0.333}O_2$" S Miao, M. Kocher, B Fultz, P. Rez, Y Ozama, R. Yazami and C.C. Ahn, ECS Meeting Abstracts, 2005, 127 (2 page)

"Does Ni change its charge state in $Li_xNi_{0.5}Mn_{0.5}O_2$", M. Kocher and P. Rez, ECS Meeting Abstracts, 2005, 128 (2 page)

"Local electronic structure of layered $Li_xNi_{0.5}Mn_{0.5}O_2$ and $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$", S. Miao, M. Kocher, P. Rez, B. Fultz, Y Ozama, R Yachimi, C.C. Ahn, J. Phys. Chem. B 109, (2006), 24374-23479.

"Local electronic structure of olivine phases of Li_xFePO_4", ", S. Miao, M. Kocher, P. Rez, B. Fultz, R Yachimi, C.C. Ahn, J. Phys. Chem. A 111, (2007), 4242-4247.

Presentations (not Previously Reported)

Miao, S. Kocher, M., Fultz, B. , Ozawa, Y. , Yazami, R., Ahn, C. C., Rez, P. , International Lithium Battery Conference, "Local Electronic Structure of Layered Lix(NiMn)O2." (May 2005).

Fultz, B. , Reynier, Y. , Swann-Wood, P. , Graetz, J., Rez, P. , Yazami, R. , Electrochemical Society Joint International Meeting, "Entropy of intercalation of Li into LixCoO2." (October 2004).

Fultz, B., Reynier, Y., Swann-Wood, P., Graetz, J., Rez, P., Yazami, R., TMS Annual Meeting, "The origin of the entropy of intercalation of Li in LixCoO2." (March 2004).

Other references

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2. Zhou,F.,Kang,K. Maxisch,T.,Ceder,G and Morgan,D. Solid State Commun, 132,1781, (2004)

3. Zhou,F,Coccoccioni,M.,Marianetti,C.A., Morgan,D.,Ceder,G. Phys. Rev B 70 235121, (2004)